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TECHNICAL MEMORANDUM No. 11/M/59

REVIEW ON Oct 89

Rates of Burning and Flame Temperatures of some Diluted Nitric Ester Monopropellant Systems

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Waltham Abbey
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October
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MINISTRY OF SUPPLY

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

TECHNICAL MEMORANDUM NO. 11/M/59

Rates of Burning and Flame Temperatures of some
Diluted Nitric Ester Monopropellant Systems

by

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1. SUMMARY

Some chemical effects of diluents in the flames of nitric ester monopropellant fuels are discussed. The nature of the diluent is important in so far as its decomposition products can influence the rate of reduction of nitric oxide in the flame gases and consequently alter the rate of heat release. The greater effectiveness of certain chemical structures with regard to nitric oxide reduction in these flames has been demonstrated and interpreted in terms of the type of radicals produced in the pyrolysis of the diluent or the products from the nitric ester itself. The pressure has an important effect on the rate of the nitric oxide reactions and the way in which the proportion of nitric oxide reduced in the flame front and in subsequent reactions varies with the pressure is examined.

The amount of any diluent that can be added before stability of combustion is impaired depends very much upon the chemical structure of the diluent. The rates of burning and flame temperatures for ethyl nitrate and isopropyl nitrate diluted with different types of coolant have been measured down to the limit of dilution in 14.7 mm tubes (pressures up to 1000 p.s.i.g.) For example about twice as much glycerol formal as n-heptane is required to reduce the flame temperature a given amount, but at high pressures (e.g., above 500 p.s.i.g. for ethyl nitrate) the rate of burning is, within a factor of about two, the same for the same flame temperature whatever the diluent.

Pyrolysis experiments at around 700°C have given an indication of the products likely to be formed from the diluents, and since the mean molecular weight of the products of the "more reactive" type of diluent (e.g., glycerol formal or dimethyl carbonate) is less than that of the paraffin type of coolant or of isopropyl nitrate itself, it would seem generally advantageous to use the "more reactive" type in a cooled monopropellant system. More glycerol formal than any other diluent can be added to isopropyl nitrate and, particularly, ethyl nitrate before flame propagation is prevented, the latter system finally giving a much lower temperature.

The burning rates of a few "more reactive" nitric esters (glycol mononitrate, methyl cellosolve nitrate and cellosolve nitrate) have been compared up to 2000 p.s.i.g.

2. INTRODUCTION

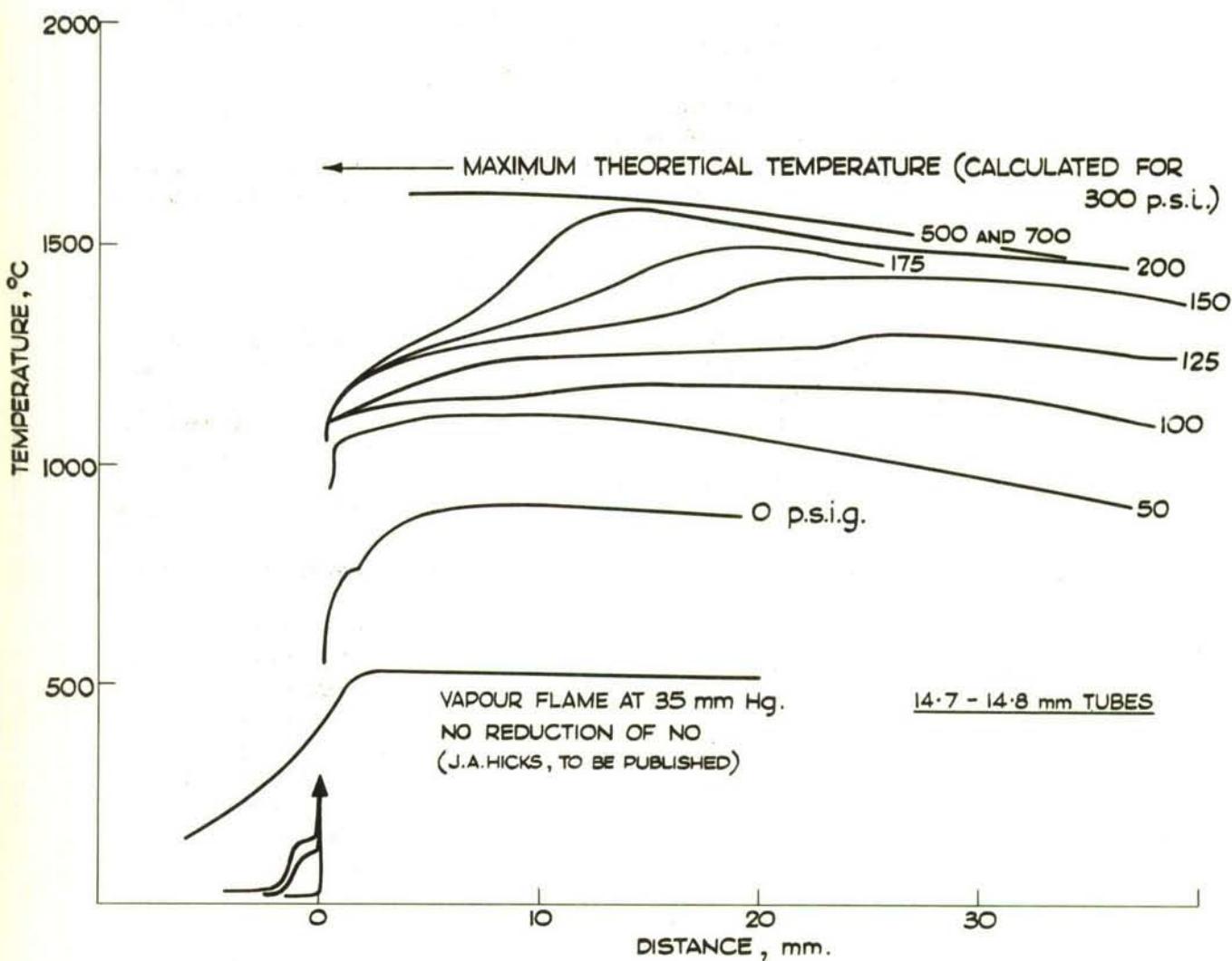
Much attention has been given to nitric ester monopropellant systems with the objective of maximum performance combined with minimum sensitiveness but, apart from the propyl nitrates, there has been little interest in the lower energy fuels. Today, there is a demand for liquid monopropellants which will burn rapidly and efficiently to produce cool and preferably "clean" gases. The latter should have as low a molecular weight as possible, and a temperature around 800°C is desirable. The range of such fuels has not been investigated at all extensively hitherto, perhaps because of the satisfactory performance of isopropyl nitrate (IPN) in systems demanding only short duration. A much cooler gas producer is desired for systems which are required to run for long periods. This paper considers some nitric ester/coolant mixtures from the chemical point of view and gives rate of burning and flame temperature data as yet unpublished.

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FLAME TEMPERATURE PROFILES FOR ETHYL NITRATE
EFFECT OF PRESSURE.

FIG. I.

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3. THE RATE OF REDUCTION OF NITRIC OXIDE IN NITRIC ESTER PROPELLANT FLAMES AND ITS EFFECT ON TEMPERATURE DISTRIBUTION AND RATE OF BURNING

It is known that the burning of nitric esters takes place in two main stages. In the first, the nitric ester is destroyed and oxidations by NO_2 and HONO take place. The reactions are complex and by no means fully understood, but recent ideas, resulting from detailed analytical studies of a number of nitric esters, have been reported, (7 - 11). Chemical reaction in this stage is incomplete in that much of the NO_2 is reduced only to NO_2 .

Final reduction of NO_2 to N_2 occurs in a later reaction which is usually too remote from the first stage to have any significant influence upon it or, consequently, upon the rate of burning of the ester. How much of the NO_2 reduction occurs in each zone at any pressure is not readily determined, but it is certain that some always takes place in the primary reaction zone (except at pressures much below atmospheric) and the extent of this reaction has an important influence on the temperature gradient and the rate of burning because of its highly exothermic nature. If a greater proportion of NO_2 reduction could be induced in the first reaction zone a higher rate of burning could be achieved for the same total energy. A corollary to this would be that, with a suitable diluent, the same rate of burning could be achieved with a lower final temperature. The delayed release of energy due to the stability of the NO_2 is demonstrated for ethyl nitrate (EN) by the temperature profiles given in Figure 1. These have been obtained by allowing the liquid to burn past a thermocouple stretched horizontally through the liquid in a 14 mm. diameter glass tube. Details of the method are given in the Appendix (p. 25). No attempt has been made to measure the high temperature gradients in the flame front, which is very difficult and requires a rather exacting technique with burning liquids (12, 13, 15), but a pressure range has been chosen so that valid measurements could be quickly and easily made of the temperature rise behind the flame front. This temperature rise genuinely reflects the course of the NO_2 reduction in the flame gases, since other pyrolyses and changes of equilibrium involve only small changes of energy. With no reduction of NO_2 at all, the flame temperature of ethyl nitrate at atmospheric pressure would not exceed $\sim 500^\circ\text{C}$. It is observed (Fig. 1) that, as the pressure rises, more NO_2 is reduced in an early fast stage (presumably in the flame front) and the rate of reduction of the remaining NO_2 increases. Some cooling is experienced by the gases in the relatively narrow tubes (14 mm.), and this should be borne in mind when inspecting the curves. In the slow phase of reaction (NO_2 reduction) the rate of heat release at, say, 100 - 200 p.s.i.g. in the 14 mm. tubes, can be of the same order as the rate of heat loss. The theoretical maximum temperature is virtually reached in these tubes at pressures above 200 p.s.i.g., whereas in 3.7 mm. internal diameter tubes pressures above 500 p.s.i.g. are necessary (13).

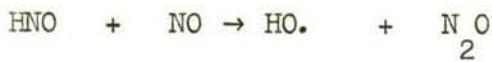
The proportion of NO_2 reduced in the primary zone depends upon the pressure, the flame temperature and the nature of the products from the initial nitric ester degradation and from any diluent present. Ideas on the mechanism of reduction of NO_2 have been formulated as a result of a study of the methyl nitrite flame (9) and of the flames of some simple nitric esters (7 - 11), and it is possible that some predictable measure of control over the rate of burning at constant energy level might be achieved by selection of diluent.

Inspection of the concentration profiles of a number of different nitric ester flames has suggested that those systems which can produce hydrogen atoms, or species which readily give up hydrogen atoms (for example, the methoxy radical), are likely to show a greater rate of reduction of NO_2 than those systems producing mainly alkyl radicals in their decompositions. Thus

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there is evidence that NO added to the methyl nitrite flame is reduced by CH_3O , and in numerous nitric esters the disappearance of NO in the hot gases behind the flame front is linked with that of H_2CO . When H_2CO is absent in the products, or when its pyrolysis is complete, the rate of reduction of NO and the rate of rise in temperature is much lower.

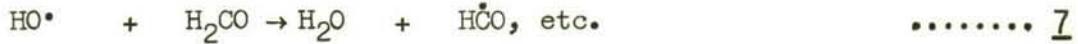


H_2CO decomposes via a hydrogen atom chain (16).

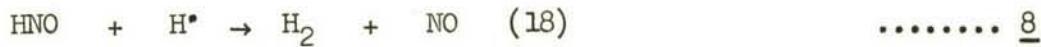


A study of this decomposition in the presence of NO at 623°C in a silica vessel has shown that small amounts of NO reduce the rate of decomposition (until all the NO has been consumed) and large amounts of NO increase the rate. With equal parts of H_2CO and NO it has been found that the rate of decomposition of NO relative to that of H_2CO increases as the total pressure of the system increases until, at ~ 500 mm. Hg, spontaneous ignition occurs (within 0.5 s.). This ignition temperature is significantly lower than those determined (17) for stoichiometric mixtures of NO with other fuels, such as NH_3 (800°C), C_2H_4 (1045°), CH_4 (1110°), H_2 (1320°) or CO (1450°), flowing through a quartz furnace with about 1 second contact time.

The NO could be reduced in the H_2CO decomposition by reactions such as:



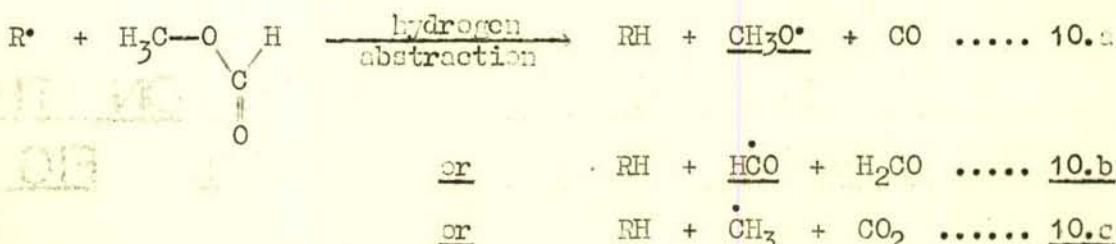
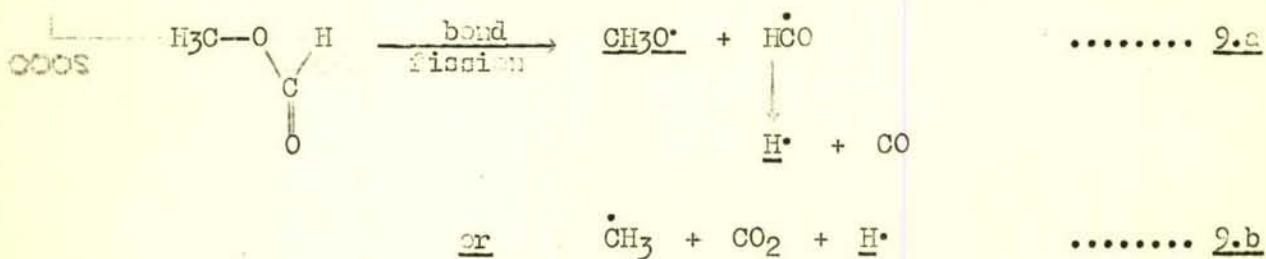
At high concentrations of NO reaction 2 might be preferred to chain terminating reactions such as 8 or 9, below.



/Although

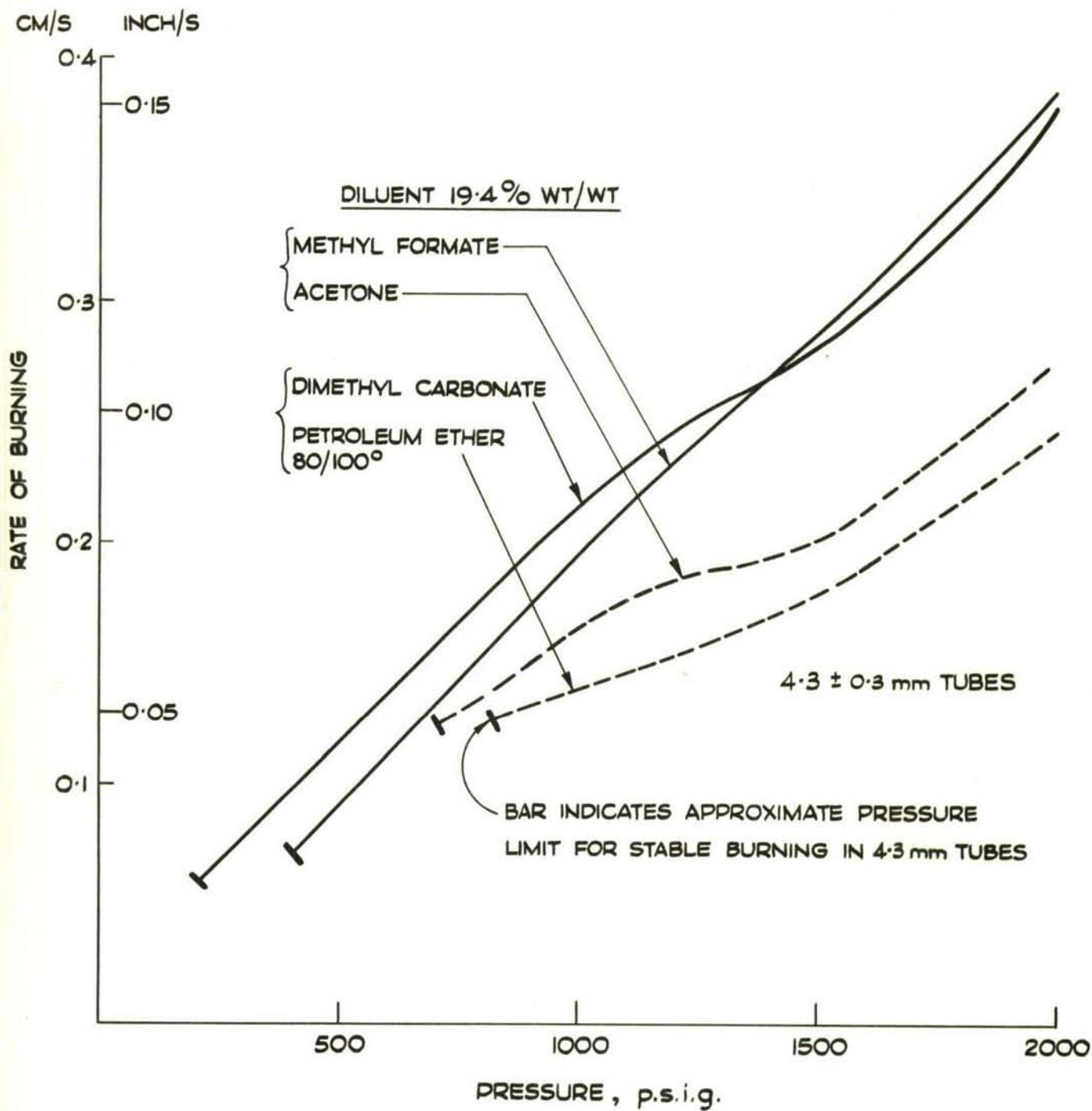
Although alkyl radicals are known to react with NO in relatively low temperature pyrolyses, they do not seem to be very effective in reducing NO at the temperatures experienced in nitric ester flames and at atmospheric pressure. Nitric oxide is not nearly so rapidly reduced in flames in which, for example, acetaldehyde is pyrolysing (10) as in flames in which H_2CO is pyrolysing. The paraffins, which decompose largely via alkyl radical chains, inhibit the burning of ethyl nitrate strongly; Adams and Wiseman (3) record the fact, for example, that the amount of n-heptane required to "desensitise" Myrol 75 (CH_3ONO_2 75%, CH_3OH 25%) is only about one-third of that of methanol, and consider possible chemical reasons for the relative efficiencies of diluents in this respect. Similarly, the effectiveness of a "coolant" added to a nitric ester will no doubt depend very much upon its chemical structure and its stability. As a tentative working hypothesis it will be said that those which might be expected on pyrolysis to give $\text{CH}_3\text{O}^\bullet$ or H^\bullet , will reduce the rate of burning less than those producing alkyl radicals, other conditions, such as heat of conversion of the liquid diluent to products, and thermal conductivity, being equal. Chemical difference between diluents might be expected to be less noticeable as the pressure, or the flame front temperature, increases beyond the values at which most of the nitric oxide is, in any case, reduced in the flame front itself. Similarly, chemical differences in the nitric esters (at constant heat of explosion) have a more marked effect on burning rate at lower pressures.

High oxygen content in an organic coolant would generally be expected to reduce the probability of alkyl radical production during pyrolysis or radical attack, but the particular location of the oxygen atom in the carbon chain is important. The actual mechanism of pyrolysis is known only for a few of the simplest molecules, but for the purpose of selection of likely coolants predictions can be made concerning more complex compounds. Consider some simple organic compounds as examples. The thermal degradation of methyl formate is a free radical process (20); the products at $\sim 730^\circ\text{C}$ are found to be 1.22 CO, 0.18 CO_2 , 0.26 CH_4 , 0.34 CH_3OH and 0.82 H_2 , (for conditions see Appendix, p.25). The limited amounts of CH_4 and CO_2 (and the absence of C_2H_6 and C_2H_4 which could also be formed, instead of CH_4 , from CH_3 radicals) indicate that, of the probable reactions listed below, those producing $\text{CH}_3\text{O}^\bullet$ and H^\bullet are preferred. Kebarle and Lossing (21) find that in the mercury-photosensitised decomposition of methyl formate the main reaction is to produce $\text{CH}_3\text{O}^\bullet$ and HCO , the formation of CH_3 and HCOO^\bullet being subsidiary.

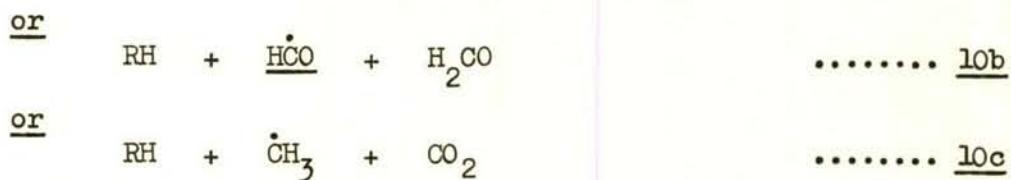


/Fig. 2
/or

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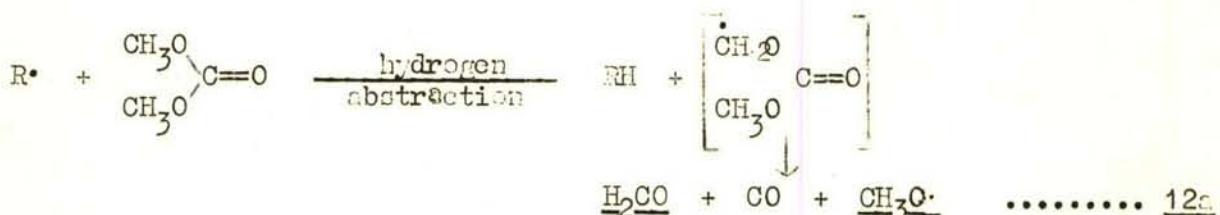
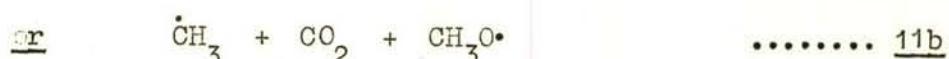
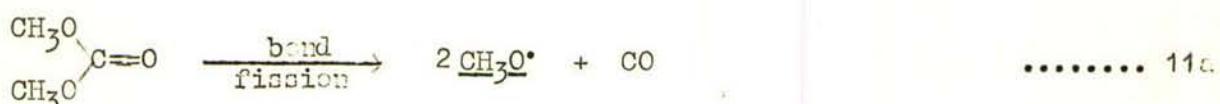


EFFECT OF NATURE OF DILUENT ON THE RATE OF BURNING OF ETHYL NITRATE. FIG. 2.



Either process produces the species (underlined) thought to be effective in reducing NO at high temperatures.

The pyrolysis of dimethyl carbonate in the region $770^\circ - 915^\circ\text{C}$ is also a free radical process (14) and the products, when the carbonate is decomposed at 730°C (for condition, see Appendix), have the following molar proportions: 1.7 CO, 0.6 CO₂, 0.7 CH₄ and 1.6 H₂. Only traces of C₂ compounds could be detected (infrared analysis). Methanol is present at lower temperatures and shorter contact times. Thus at 660°C the following analysis was obtained: 1.62 CO, 0.47 CO₂, 0.76 CH₄, 0.87 H₂, 0.3 CH₃OH and 0.02 (CH₃O)₂CO. Although $\dot{\text{CH}}_3$ radicals are probably involved in the decomposition (giving rise to the CH₄), many other species capable of exothermic reduction of NO will be produced in the course of the decomposition reactions:

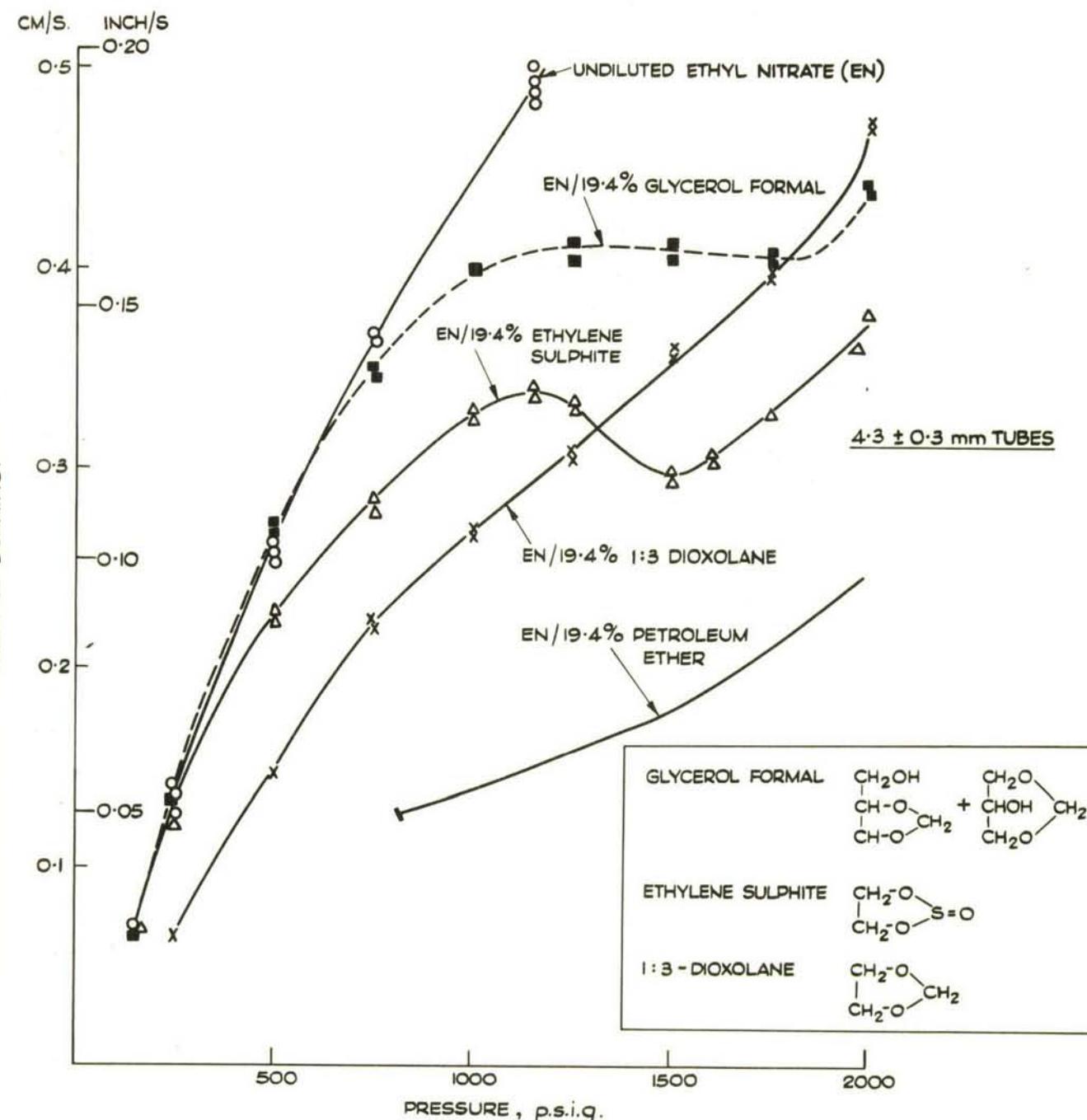


These can be compared with the pyrolysis of acetaldehyde, or acetone (see (22) and Appendix), in which only radicals unreactive towards NO at high temperatures are involved; the main reactions being:

/Fig. 3

/ $\dot{\text{CH}}_3$

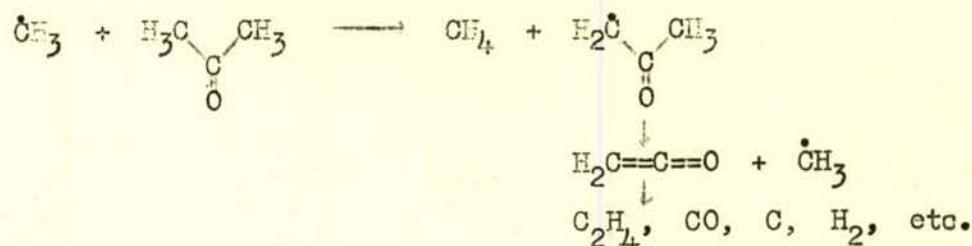
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EFFECT OF NATURE OF DILUENT ON RATE
OF BURNING OF ETHYL NITRATE.

FIG. 3.

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On the basis of the ideas put forward, a given weight of methyl formate or methyl carbonate should reduce the rate of burning of nitric esters less than the same weight of an organic compound which pyrolyses via an alkyl radical mechanism, e.g., CH_3CHO , $(\text{CH}_3)_2\text{CO}$ or a paraffin. An interesting comparison can be made between the diluents methyl formate and acetone, and between dimethyl carbonate and a petroleum ether or n-heptane. Table 1 compares some significant properties of the two pairs of coolant.

TABLE 1

Coolant	CH_3OCHO	$(\text{CH}_3)_2\text{CO}$	$(\text{CH}_3\text{O})_2\text{CO}$	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$
B.p., °C:	31.5	56.5	90-91	98.5
Density (g./ml., 20°C):	(15) 0.91	0.792	1.069	0.684
Heat of Vaporisation (at b.p.), cal/g.:	112	124	88	80
Heat Capacity, cal/g. deg.C.:	0.516	0.506	0.45	0.5
Heat Absorbed on Conversion to Products Below, cal/g.:	375(a)	280(b)	290(c)	390(d)
Mean Heat Capacity of Products 25° - 1000° C, cal/g.	0.45	0.57	0.46	0.64

* Products of decomposition assumed to be the same as those found from pyrolysis experiments at 700° (see Appendix):

- (a) 1.22 CO + 0.18 CO₂ + 0.26 CH₄ + 0.34 CH₃OH + 0.82 H₂
- (b) 1.01 CH₄ + 0.86 CO + 0.07 CO₂ + 0.10 C₂H₄ (+ 0.83 C + 0.78 H₂)
(C and H₂ assumed for balance)
- (c) 1.69 CO + 1.6 H₂ + 0.7 CH₄ + 0.6 CO₂
- (d) 0.8 CH₄ + 0.04 H₂ + 0.88 C₂H₆ + 1.41 C₂H₄ + 0.34 C₃H₈ + 0.42 C₃H₆ (25)

(Equilibrium calculations would not be worth while, since equilibrium is not attained in practice).

/The

The rates of burning of 19.4 per cent (w/w) mixtures of ethyl nitrate with each of these diluents are shown in Figure 2. Large differences are observed in rate of burning and in the minimum pressure at which the mixture will continue to burn in the 4.3 ± 0.3 mm. diameter glass tubes.

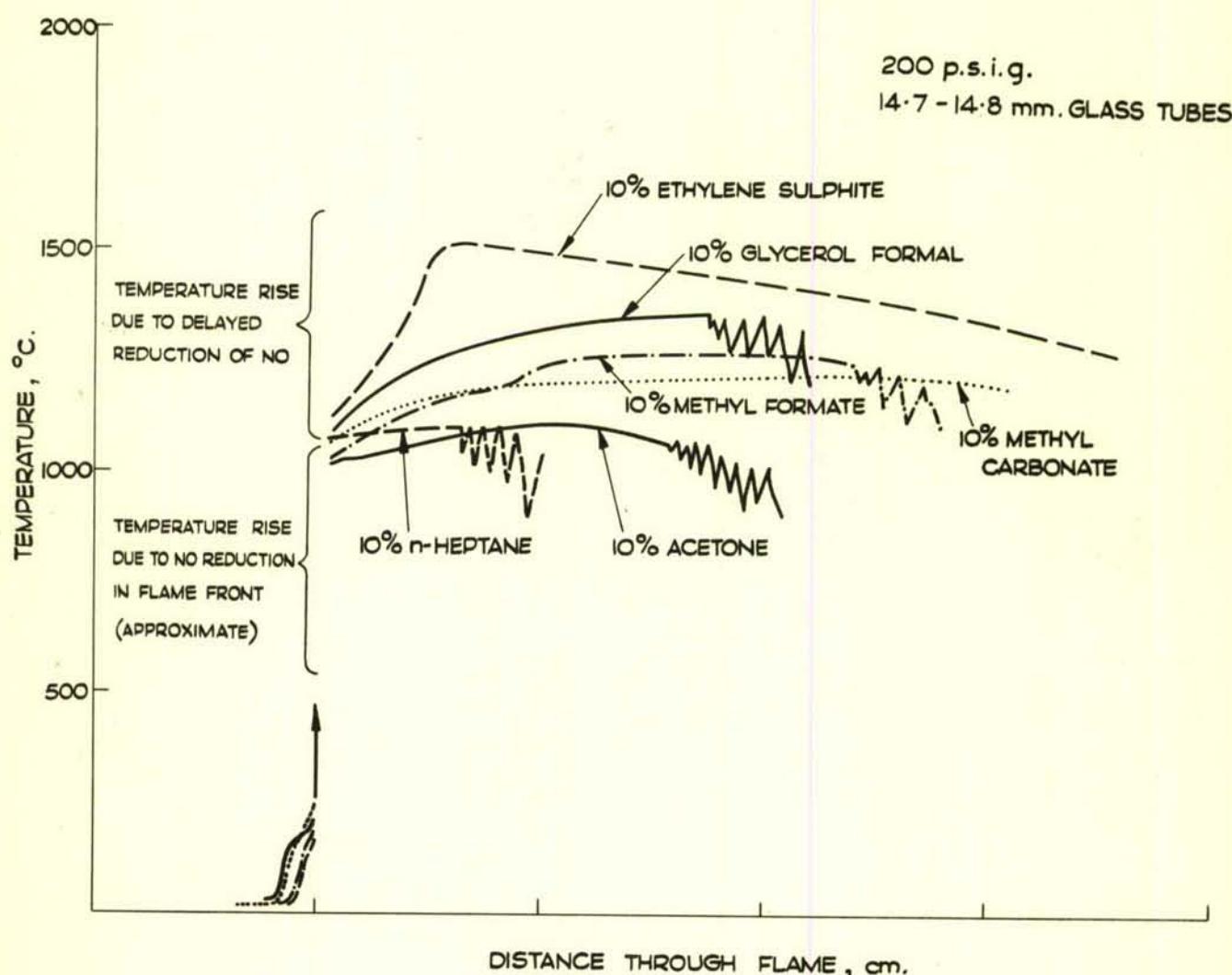
At atmospheric pressure, in 24 mm. tubes, the rate of burning of ethyl nitrate is reduced from 0.0074 cm/s. to 0.0048 cm/s. by diluting with 9.8 per cent (w/w) dimethyl carbonate, 9.0 per cent methyl formate or 9.3 per cent methanol; only 3.5 per cent of petroleum ether (b.p. $100^{\circ} - 120^{\circ}\text{C}$) is required for a similar reduction in rate. The maximum temperatures recorded for these mixtures did not differ greatly; they were 812° , 816° , 790° and 784°C respectively.

Paraformaldehyde was not readily soluble in the nitric esters, but some compounds which might be expected to eliminate H_2CO during pyrolysis or to decompose in a similar fashion to H_2CO have been compared with a paraffin in Figure 3. The rates of burning with all three compounds are very much higher than those of the petroleum ether or acetone mixtures. The sinuous burning rate curves for EN/glycerol formal and EN/ethylene sulphite in 4 mm. tubes show very remarkable features which initially aroused much interest, but which later only revealed further shortcomings of attempting to determine liquid burning rates in small diameter tubes. The rates of burning of the EN/19.4 per cent glycerol formal mixtures and the EN/19.4 per cent ethylene sulphite mixtures at 500 p.s.i.g. are, in fact, much lower in the 14 mm. tubes than in the 4.3 mm. tubes. This must be due to some unknown anomalous effect of the tube, involving, perhaps, the viscous drag on the liquid. The effects of confinement of the liquids in tubes have been considered from time to time and recently, for ethyl nitrate, a detailed analysis has been made (23), but much still remains to be learned about the effect of viscosity, surface tension, wall-quenching and convectional cooling of gas and liquid (to name a few of the important factors) before determination of a fundamental rate of burning of a liquid can be made from measurements in narrow tubes. Although it is normally necessary to determine rates in small capacity systems (with liquid explosives more so than with solids), much reserve should be exercised in the interpretation of detailed behaviour. The rates of burning of these mixtures as a function of pressure have not been determined in 14 mm. tubes.

Another method by which the effectiveness of diluents upon NO reduction can be compared is to observe the rates of temperature rise behind the flame front at some pressure selected as suitable for unequivocal

/temperature

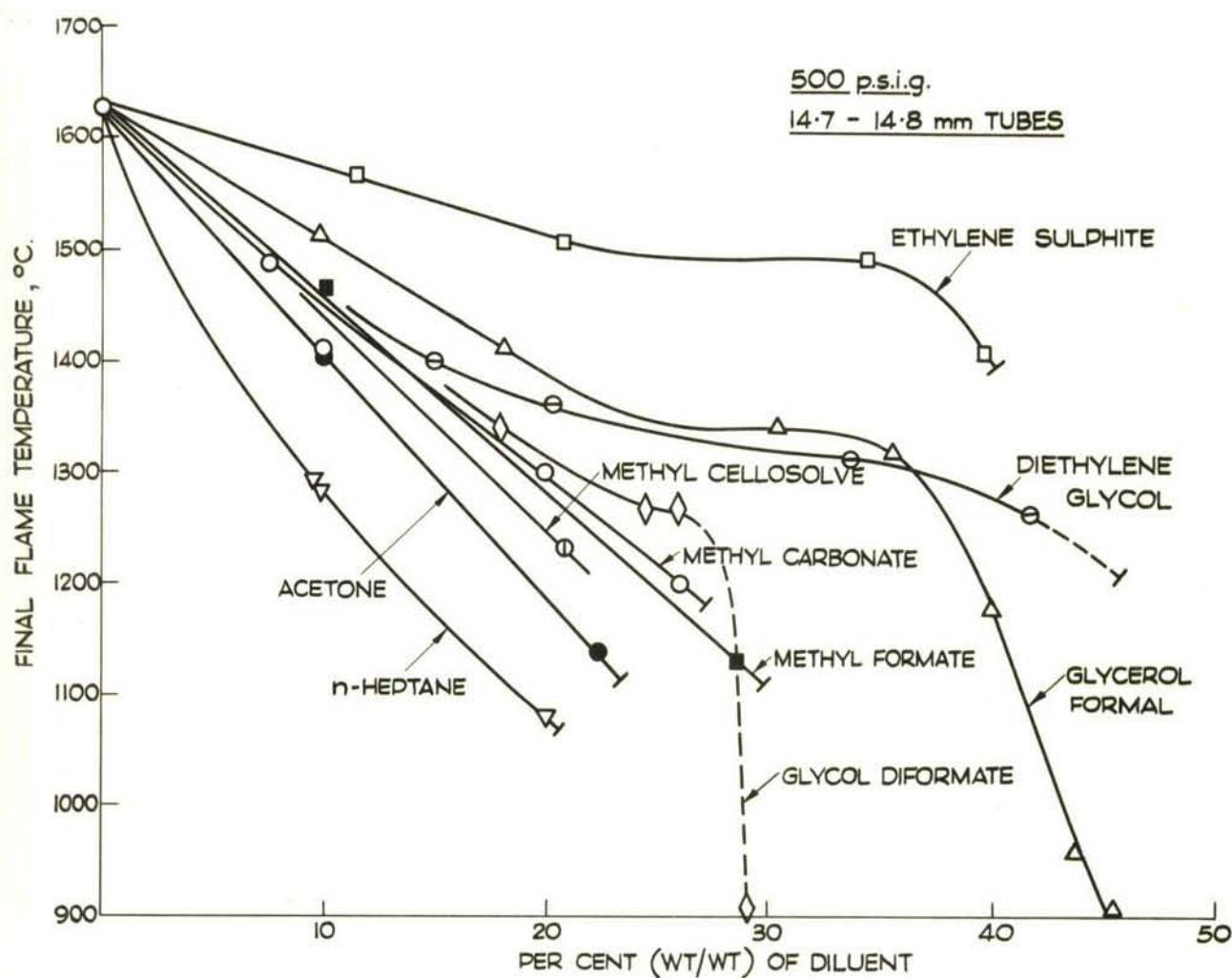
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TEMPERATURE DISTRIBUTION IN ETHYL NITRATE / DILUENT
10% (WT/WT) FLAMES.

FIG. 4.

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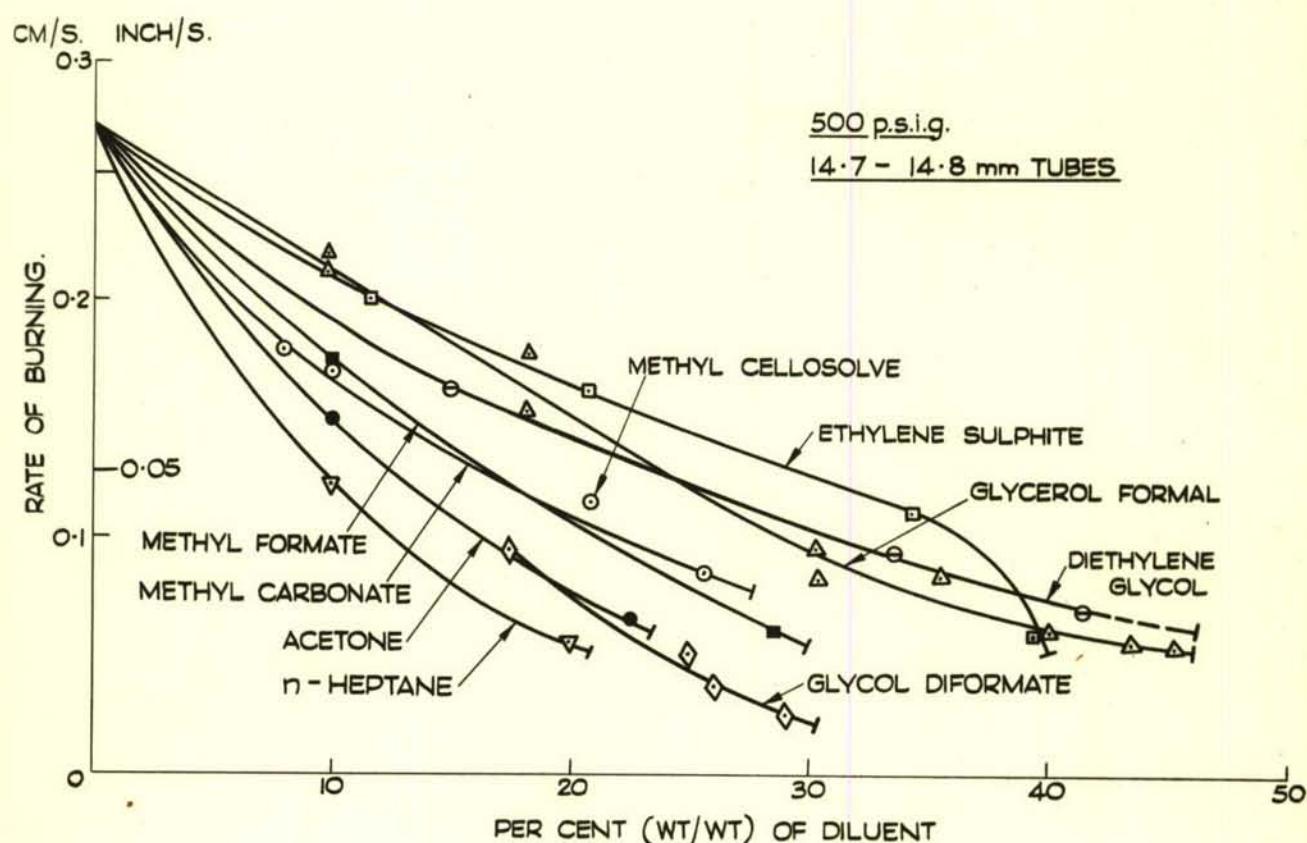


FLAME TEMPERATURES OF DILUTED ETHYL NITRATE.

FIG. 5.

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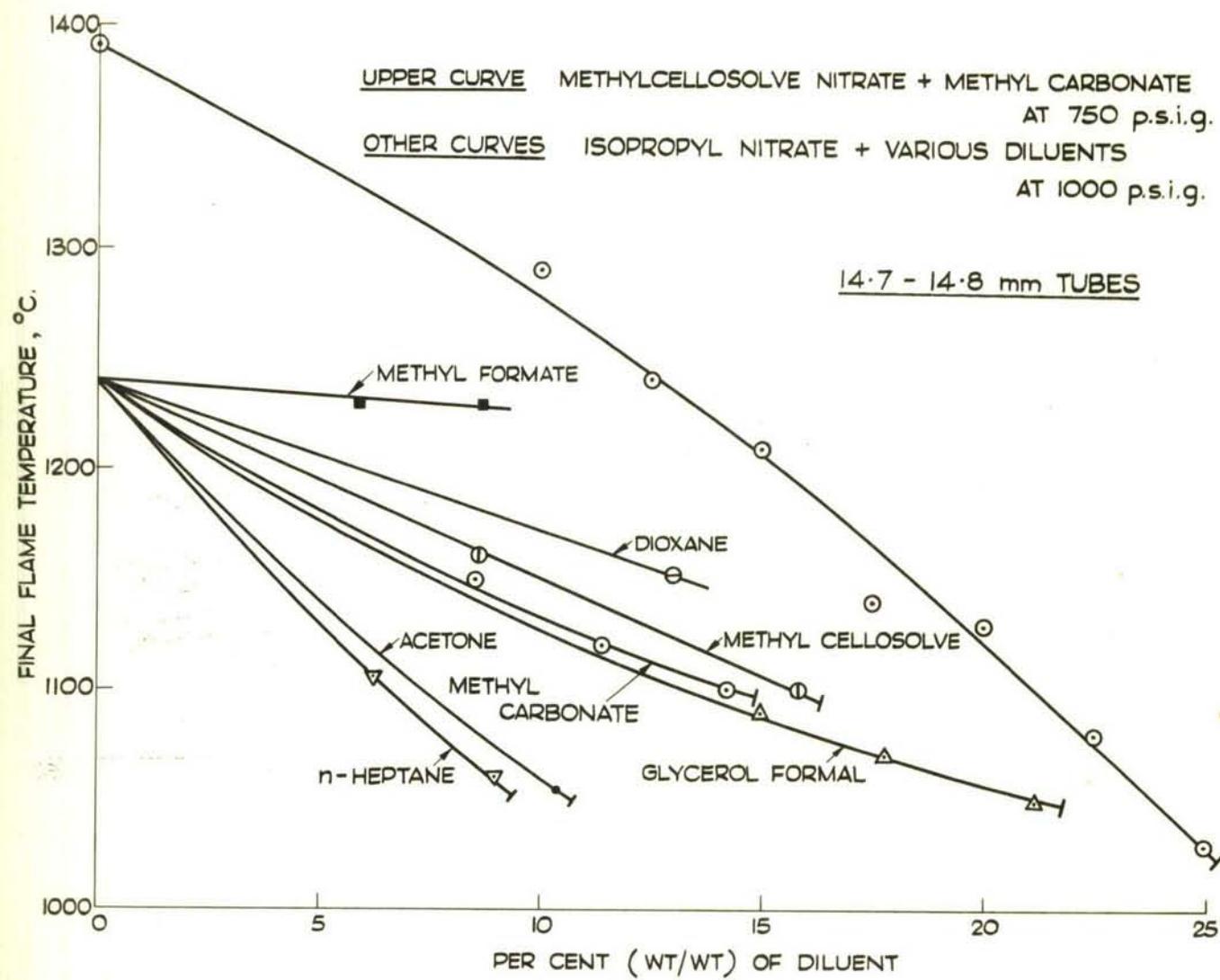


RATES OF BURNING OF DILUTED ETHYL NITRATE.

FIG. 6.

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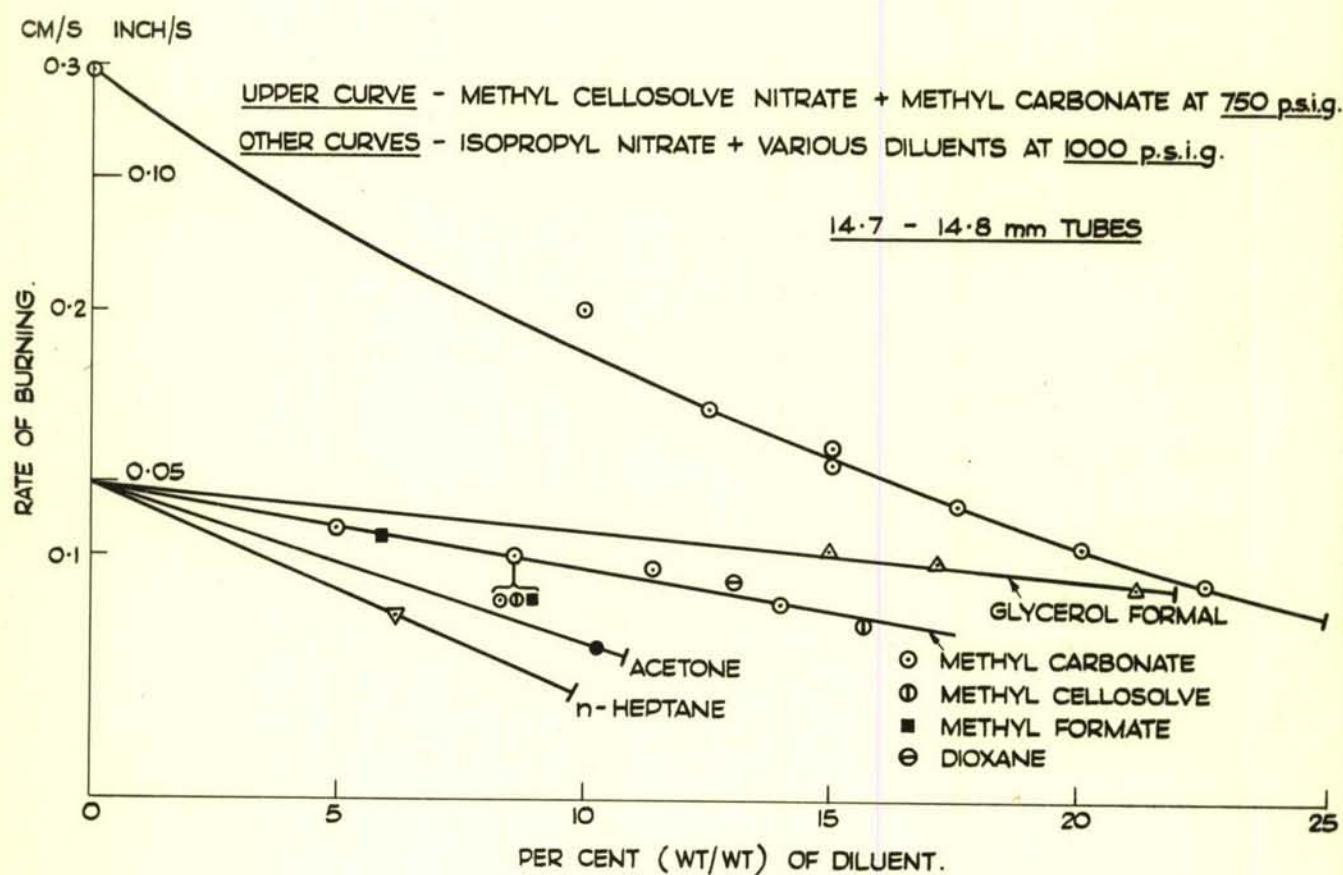


FLAME TEMPERATURES OF DILUTED ISOPROPYL AND
METHYLCELLOSOLVE NITRATES.

FIG. 7.

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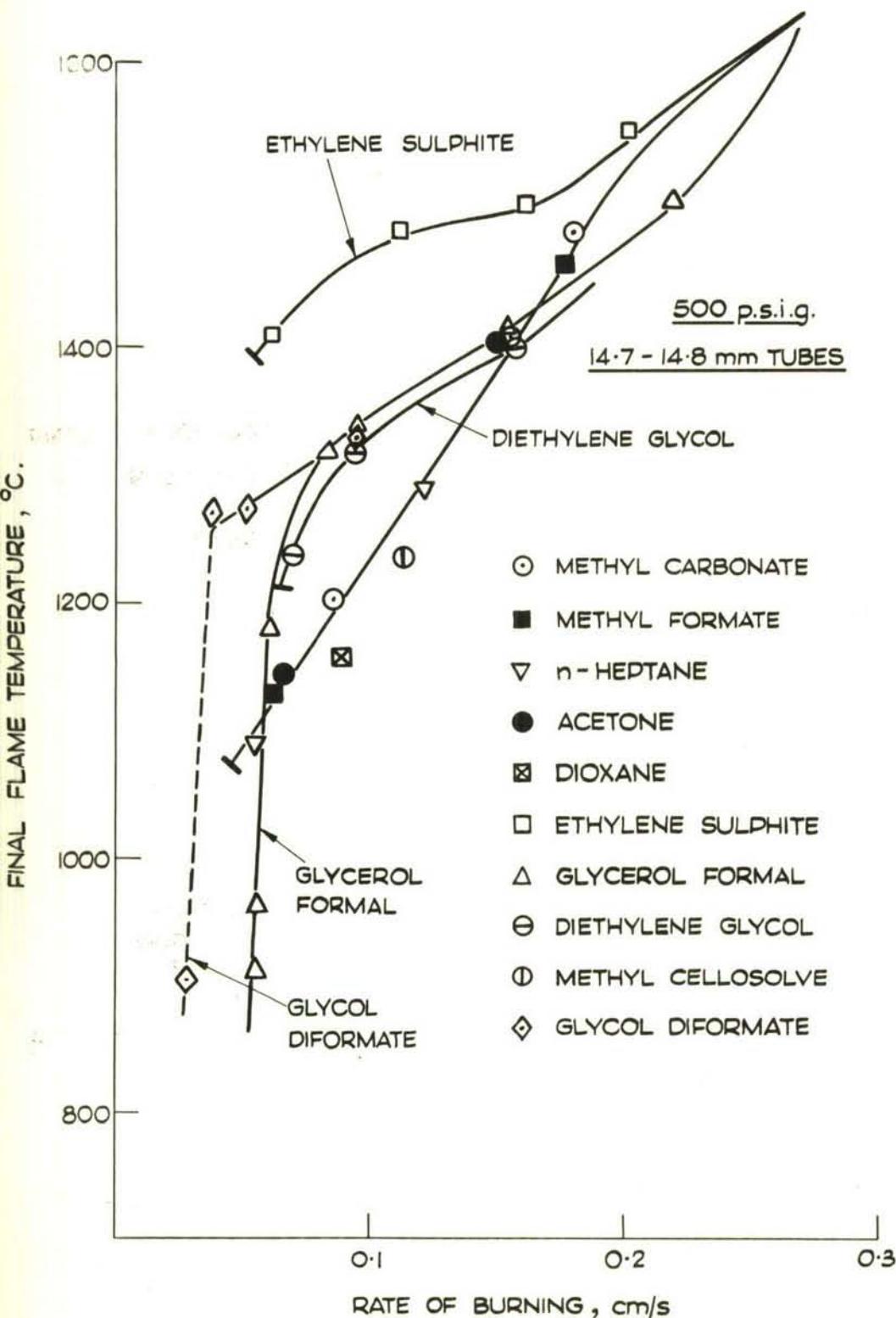


RATES OF BURNING OF DILUTED ISOPROPYL AND
METHYL CELLOSOLVE NITRATES.

FIG. 8.

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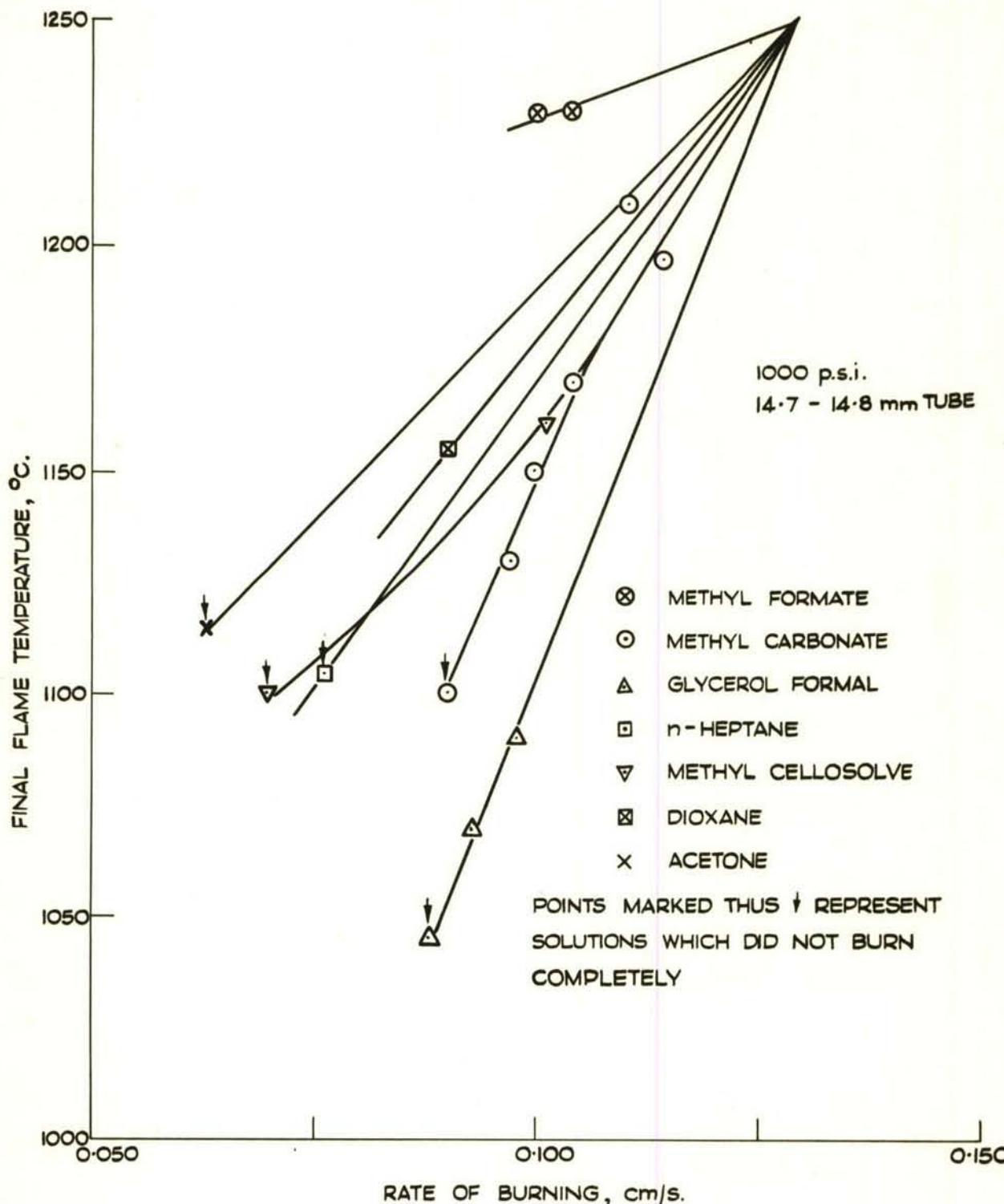
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FINAL FLAME TEMPERATURE AND BURNING RATE
FOR DILUTED ETHYL NITRATE.

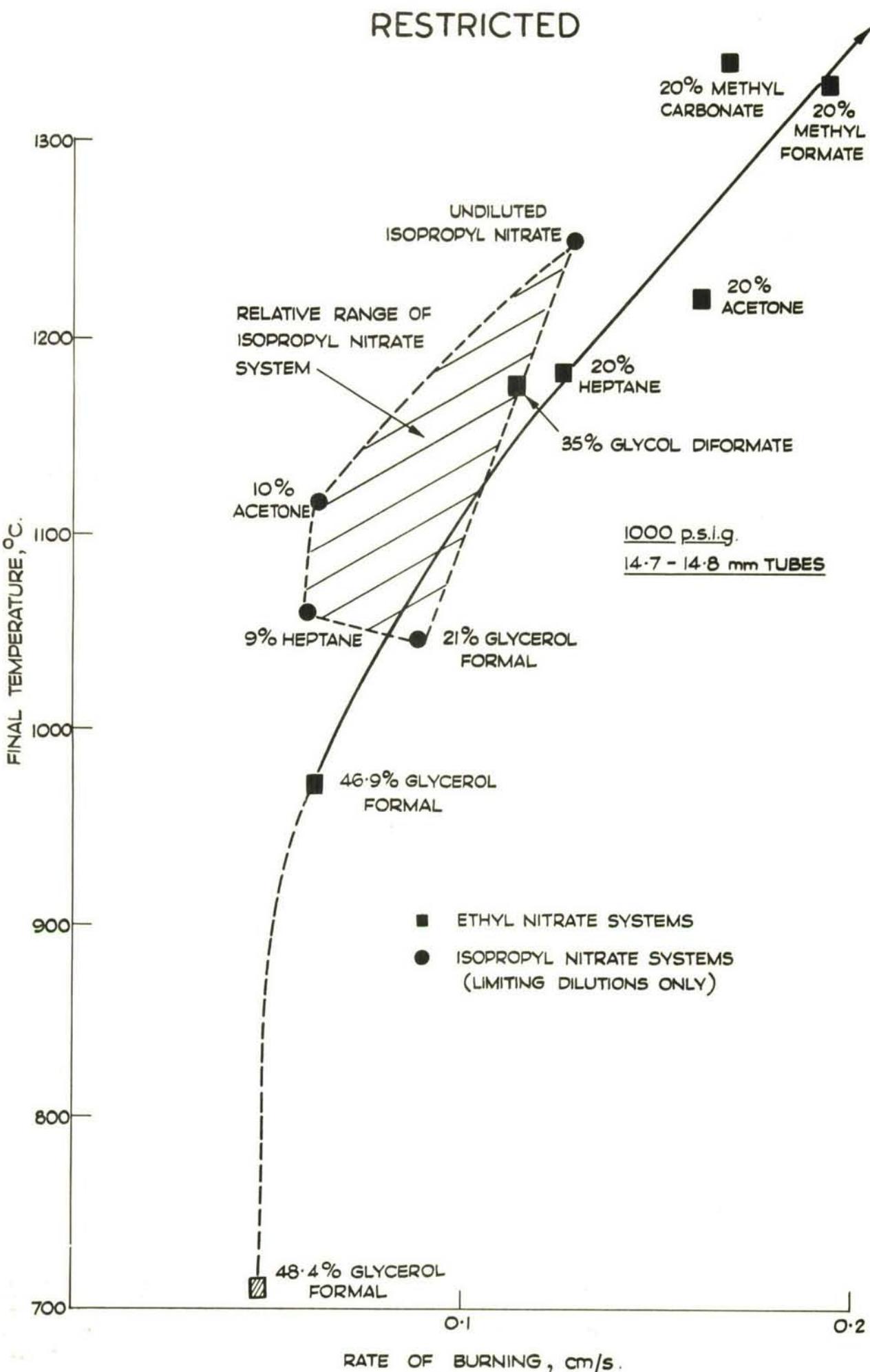
FIG. 9

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FINAL FLAME TEMPERATURE AND BURNING RATE
FOR DILUTED ISOPROPYL NITRATE.

FIG. 10.



A COMPARISON OF FLAME TEMPERATURES AND RATES OF BURNING FOR ETHYL NITRATE AND ISOPROPYL NITRATE SYSTEMS.

FIG. II

temperature/time measurements. A suitable pressure for comparison of ethyl nitrate/10 per cent (w/w) diluent mixtures is about 200 p.s.i.g., and the temperature profiles in Figure 4 show that methyl formate and methyl carbonate do, under these conditions, give more rapid heat release than n-heptane or acetone. Ethylene sulphite and glycerol formal are found to be superior in this respect to both methyl formate and dimethyl carbonate.

4. FLAME TEMPERATURE AND RATES OF BURNING OF DILUTED NITRIC ESTERS

The above diluents, and a number of others, have been compared in ethyl nitrate and isopropyl nitrate at the fixed pressures of 500 p.s.i.g. and 1000 p.s.i.g. respectively. A limited amount of information has been obtained for methyl cellosolve nitrate ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{ONO}_2$) at 750 p.s.i.g. These pressures were selected so that it was possible to measure, over a range of nitric ester/diluent compositions, the rate of burning and the flame temperature in 14.7 mm. tubes, whilst the pressures are in the practical working range. The response of the thermocouple and recorder were inadequate to detect much structure in the temperature profiles at the burning rates usually encountered at these pressures. It is likely that most of the nitric oxide is reduced in the flame front; some delayed temperature rise could be observed for the cooler ethyl nitrate mixtures and most of the isopropyl nitrate mixtures, but it was not large. The maximum dilution for stable burning has been determined for most of the coolants. This limiting concentration applies only to the conditions of these experiments, but the relative behaviour of the coolants should be the same with a given nitric ester under other conditions.

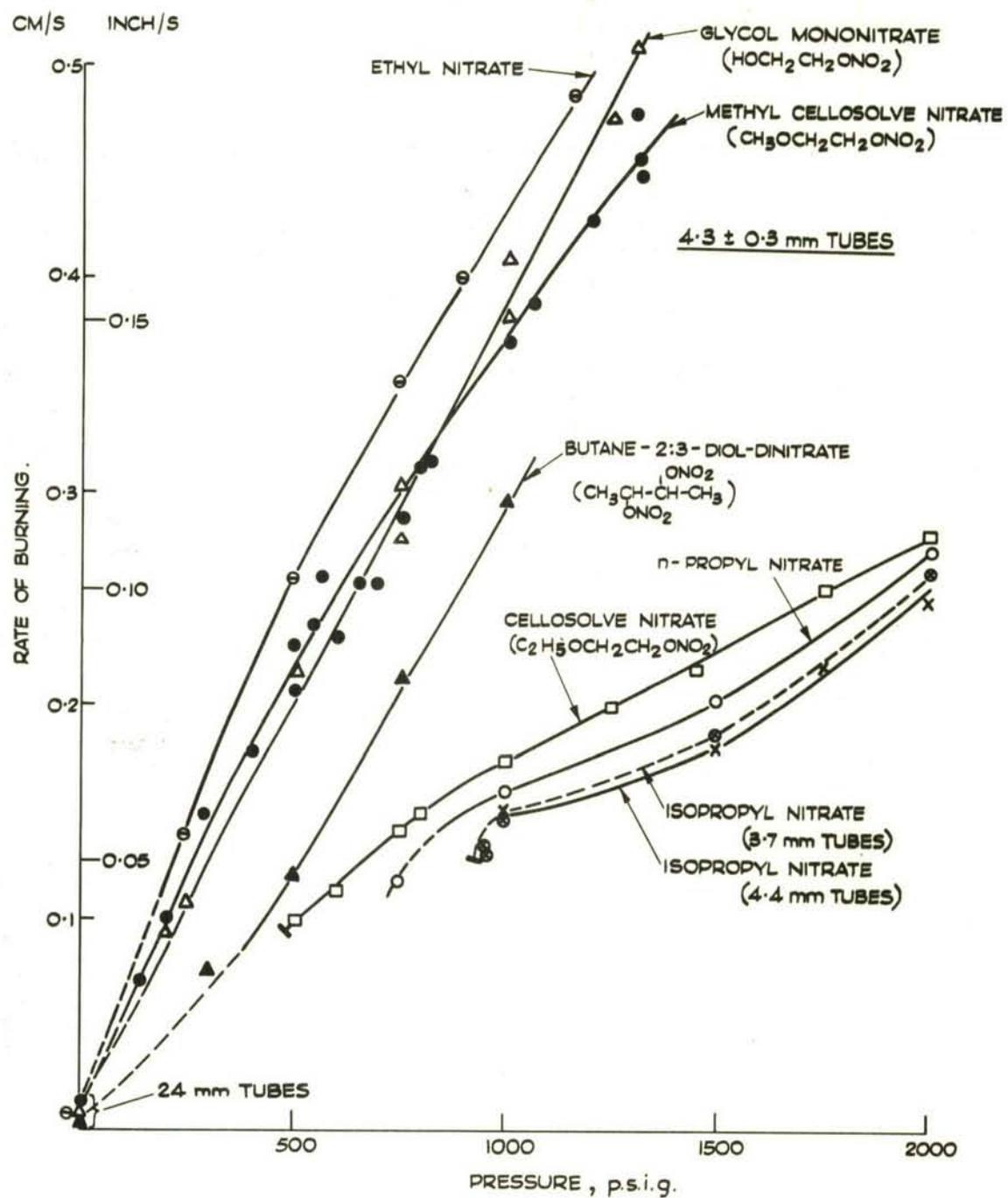
The flame temperatures and the rates of burning of diluted ethyl nitrate, isopropyl nitrate and methyl cellosolve nitrate as a function of the weight of diluent added are summarised in Figures 5, 6, 7 and 8. The dilution limits for stable condition under the conditions employed are indicated on the curves; much more dilute mixtures can be made to burn in larger reactors. The Special Propulsive Section, I.C.I., have been able to reduce the gas temperature of isopropyl nitrate to as low as 615°C with certain diluents and still maintain stable combustion at 350 - 400 p.s.i.g. (24). The characteristic chamber length was large, 5600 inches. A similar order of effectiveness in cooling the products is found for diluents common to the I.C.I. tests and the present experiments. Figures 9 and 10 show the relationship between the rate of burning and the maximum temperature recorded during the burning of diluted ethyl nitrate (at 500 p.s.i.g.) and isopropyl nitrate (at 1000 p.s.i.g.), irrespective of the actual quantity of diluent required to give the reduced temperature. In the ethyl nitrate system the correspondence between rate and maximum temperature is, at this pressure, similar for all the diluents except ethylene sulphite, glycerol formal and diethylene glycol, which show the same form of anomalous behaviour (Figure 9). Fewer measurements have been made with isopropyl nitrate mixtures, some dilution limits only being determined.

A comparison of ethyl nitrate and isopropyl nitrate systems at the same pressure is made in Figure 11. The temperature range of isopropyl nitrate mixtures is limited and, although for the same flame temperature (at these high pressures) the rates in the two systems are not very different, it would appear that ethyl nitrate can be diluted to much lower temperatures, at least with the more reactive coolants.

/Fig. 12

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THE RATE OF BURNING OF SOME NITRIC ESTERS. FIG.12

5. RATES OF BURNING OF SOME NITRIC ESTERS

The rates of burning of some substituted ethyl nitrates have been obtained; they are compared in Figure 12 with those of some more common nitric esters burning under identical conditions (4.3 ± 0.3 mm. glass tubes), and may be considered a minor addition to the extensive liquid burning rate data previously obtained by Stocks (1,2,4), Wiseman (1,3) and Adams (4,6). As has been pointed out by the latter authors, the rates are not necessarily in line with the heats of explosion of the esters, and the ease of ignition and lower pressure limits of stable burning also depend very much on the particular chemical structure of the nitric ester. There should be a number of nitric esters which will burn with stability at lower temperatures than the propyl nitrates, but it may be doubted whether these would offer any overall advantage over suitably diluted EN or IPN.

6. GENERAL CONCLUSIONS

The same reduced flame temperature can be obtained by widely different weight additions of diluents, depending upon the chemical structure of the latter. Within a factor of about two, however, the same rate of burning is obtained for the same flame temperature irrespective of the nature of the diluent, the temperature being measured under non-adiabatic conditions.

The chemical differences in diluent or nitric ester probably become less significant as the pressure and the flame temperature increase, equilibrium conditions being more rapidly attained. Thus at atmospheric pressure a paraffin may be about three times as effective as, for example, methyl carbonate in reducing the temperature or the rate, whilst at 1000 p.s.i.g. it will only be one and a half times as effective. Also, it is only at very high pressures that the rate of burning of nitric esters of different structures tend to come into line with their heats of explosion.

It is anticipated that advantages in ignitability and characteristic chamber length (L^*) will be found for the more reactive diluents or nitric esters in cool monopropellants. For a restricted L^* it would be possible to lower the temperature of the flame gases with much smaller amounts of the "less reactive" type of diluent because some reaction has been inhibited. Under these circumstances, there would be a risk of erratic burning should a change of pressure or of other conditions increase the degree of chemical reaction. Further chemical reaction might conceivably take place beyond the chamber, for example on a catalytic surface, in some of the applications visualised. In any case, there would seem to be no point in using the paraffin type of diluent, because the mean molecular weight of the products from the "more reactive" type (e.g., glycerol formal, dimethyl carbonate) is lower, and, if anything, a better performance may be expected for the same gas temperature. The mean molecular weights of the products from these diluents are expected to be less than that of isopropyl nitrate products and similar to that of ethyl nitrate products, so it would seem advantageous to use ethyl nitrate highly diluted with the appropriate diluent rather than isopropyl nitrate with smaller amounts of the diluent. There should be no significant difference in hazard between the two low energy systems designed to give the same gas temperature. The relative stabilities of the diluted systems would have to be considered.

From the point of view of the "cleanness" of the gases produced, the indications from the laboratory combustions are that, although all the very cool-burning mixtures deposit tarry materials on chilled surfaces, the

/deposits

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deposits were worse with the paraffin type of diluent. As would be expected, the latter gave rise to much soot at higher pressures.

7. FURTHER WORK

The results and ideas presented in this work obviously need to be tested under more practical conditions, and motor firings of candidate mixtures for cool monopropellants suggested from the laboratory work are in progress. Gas temperatures and performances at different characteristic chamber lengths will be measured for ethyl nitrate and isopropyl nitrate solutions. Information on relative ease of ignition and on combustion products will be gathered where possible.

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/Fig. 13/14

/Appendix

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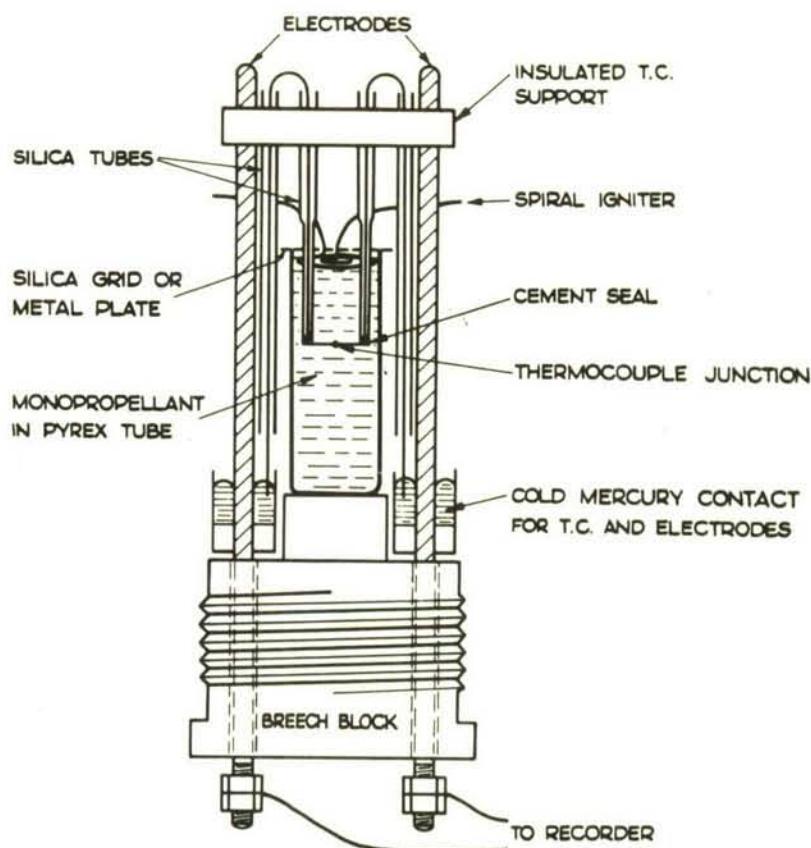
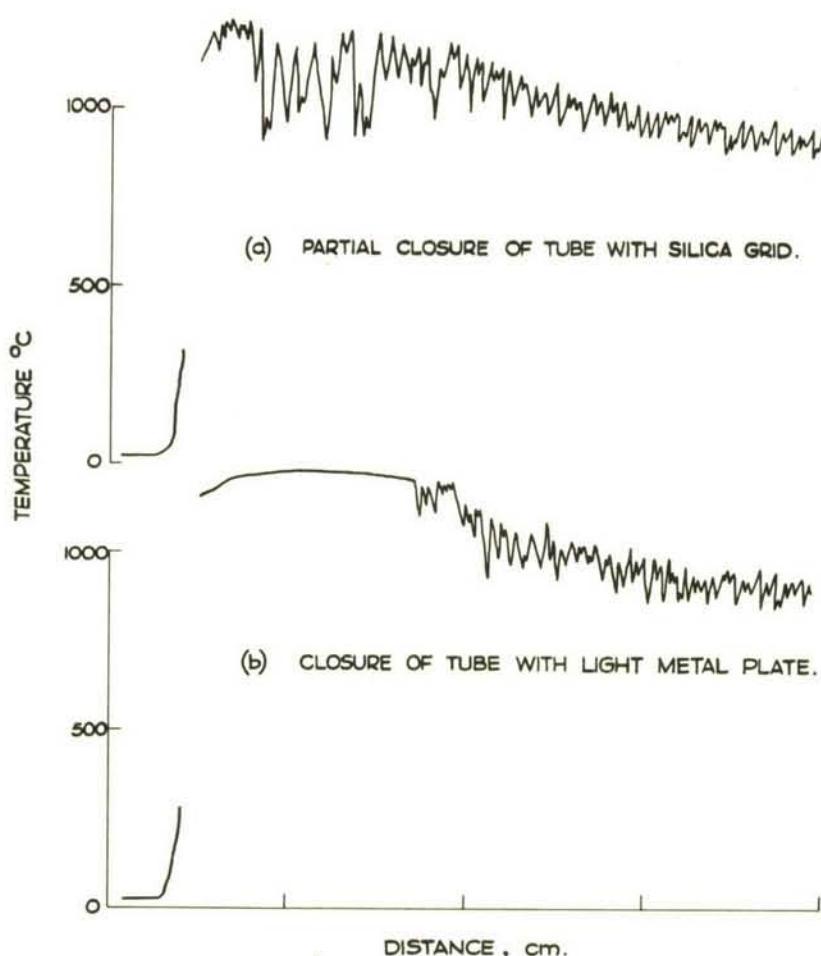


FIG. 13.



TEMPERATURE TRACES. ISOPROPYL NITRATE
IN 14.7 mm. TUBES.

FIG. 14.

APPENDIX

Measurement of Temperature Profiles and Burning Rates

Figure 13 depicts the experimental arrangement used to obtain temperature profiles and rates of burning. The liquid propellants, contained in pyrex tubes, were burned in a vessel pressurised with nitrogen, and the gas temperatures measured by allowing the liquids to burn down past a thermocouple suspended inside the tubes. The 0.002-inch diameter Pt/Pt-10 per cent Rh thermocouple was supported by thin silica tubes through which the wires were threaded. The ends of the tubes were sealed with fireproof cement to prevent entry of propellant which tended to explode if retained in the restricted tubes. A simple metal clamping device held the silicatubes between two of the four insulated electrodes with which the breech block of the vessel was fitted, these electrodes also serving (via mercury contacts) to convey the e.m.f.s from the thermocouple to a recording millivoltmeter.

Difficulties which were initially encountered in igniting some of the cooled monopropellants in wide tubes were overcome by using a spiral igniter constructed from nichrome tape, so that a large area of the liquid surface could be heated. It was found that the slower burning liquids, which were the ones difficult to ignite, gave temperature profiles which showed rapid fluctuations. The form of these profiles suggested that the velocity of the product gases passing up the tube from the burning liquid surface was insufficient in some cases to prevent the ingress of the pressurising nitrogen by convection, the cold gas passing down the inner side of the tube until it became entrained in the hot product gases. Total extinction of the flame after ignition was sometimes experienced, apparently as a result of this cold gas flow reaching the liquid surface and, in such cases, a considerable improvement was brought about by placing a silica grid or a light metal plate over the mouth of the tube to restrict the flow of gas to that of the products passing out of the tube. The effect of these modifications on the temperature traces is shown in Figure 14. Isopropyl nitrate could not be ignited at this pressure without restriction of the mouth of the tube. Visual observation of the burning liquids was usually impossible because of fog formation in the pressurising bomb. The rates of burning were therefore determined from the temperature recordings; the distance between the thermocouple junction and the bottom of the tube was known and the time taken for the burning surface to traverse it could be estimated from the temperature profile. It was found that the error in timing by this method was not more than ± 1 per cent.

Pyrolysis Experiments

The products of decomposition of the coolants were not always known and experiments were conducted to give some idea of the nature and relative amounts of the products formed at temperatures in the region of 700°C .

The materials were evaporated into a nitrogen stream and passed through a 25 cm. x 1.5 cm. diameter silica tube heated to the required temperature in an electric furnace. The dilute products were passed directly into cells for infrared analysis and samples were taken for mass spectrometric or gas chromatographic analysis. Rapid estimation of the products formed under these conditions could be made. Careful experimentation (e.g., with regard to temperature control and contact time) would be uneconomic, since pyrolyses under these conditions cannot be expected to give quite the same products as decomposition in a flame at high pressure. However, a useful guide to the course of the thermal degradation and the likely products of the reaction in the cooled nitric ester flames can be obtained from these experiments.

The products of the various coolants are tabulated overleaf.

TABLE 2

Coolant	Molecular Weight	Pyrolysis Temperature, °C	Products				Total Number of Moles per Mole of Coolant	Mean Weight of Gaseous Products
			H ₂ (a)	CO	CH ₄	C ₂ H ₄		
Dimethyl carbonate	90	730	1.59	1.70	0.72	trace	0.60	19.5
Glycerol formal	104	660	1.11	2.17	0.78	0.34	0.40	21.6
Ethylene sulphite	108	660	0.37	1.05	0.39	0.26	0.33 (H ₂ S = 0.35) (SO ₂ = 0.65)	31.8
Methyl formate	60	730	0.82	1.22	0.26	-	0.18 CH ₃ OH = 0.34	20.5
Acetone	58	730	0.78	0.86	1.01	0.10	0.07 C = 0.83 (c)	18.3
n-Heptane (25)	100	530	0.04	-	0.80	1.41	- C ₂ H ₆ = 0.58 C ₃ H ₈ = 0.34 C ₃ H ₆ = 0.42	27.2
Glycol diformate	118	730	0.57	2.54	0.89	0.05	0.46 H ₂ O = 0.54	5.05
								23.4

Notes a. Hydrogen figures obtained from atom balances.

b. H₂S detected by its odour in the products. Amount present was insufficient for detection by I.R. analysis. Figure obtained from atom balance.

c. Carbon was deposited on walls of reaction vessel. Amount obtained from atom balance.

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Memorandum No. 11/M/59Rates of Burning and Flame Temperatures of
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J. Powling and W.A.W. Smith Oct., 1959

Some chemical effects of diluents in the flames of nitric ester monopropellant fuels are discussed. The nature of the diluent is important in so far as its decomposition products can influence the rate of reduction of nitric oxide in the flame gases and consequently alter the rate of heat release. The greater effectiveness of certain chemical structures has been demonstrated and interpreted in terms of the type of intermediates produced on pyrolysis.

The rates of burning and flame temperatures for ethyl nitrate and isopropyl nitrate diluted with different types of coolant have been measured down to the limit of dilution in 14 mm. diameter tubes. The burning rates of a few "more reactive" nitric esters (glycol mononitrate, methyl cellosolve nitrate and cellosolve nitrate) have been compared up to 2000 p.s.i.g. pressure.

The laboratory experiments indicate that, for cooling nitric ester monopropellants, the more reactive type of diluent (e.g., glycerol formal, dimethyl carbonate) is generally more advantageous than the less reactive paraffin type, and that ethyl nitrate may be diluted to lower temperatures than isopropyl nitrate.

26 pp., 14 fig., 2 tables

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